On the equipartition of kinetic energy in an ideal gas mixture

L. Peliti

Dipartimento di Scienze Fisiche, INFN–Sezione di Napoli, CNISM–Unità di Napoli
Università "Federico II", Complesso Monte S. Angelo, 80126–Napoli (Italy)

E-mail: `peliti@na.infn.it`

Abstract. A refinement of an argument due to Maxwell for the equipartition of kinetic energy in a mixture of ideal gases with different masses is proposed. The argument is elementary, yet it may work as an illustration of the role of symmetry and independence postulates in kinetic theory.

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1. Introduction

The intuitive appeal of the classical kinetic theory of gases in the teaching of the basics of statistical mechanics is undeniable. However, one often finds that it is hard to continue along the kinetic trail without becoming entangled either in too difficult mathematics, or in too subtle arguments, which make the subject less glamorous than it should. I found the sections of the Feynman lectures dedicated to the kinetic theory [1, secs. 39, 40] remarkable in balance and scope, in the attempt to derive the essentials of the Gibbs approach to statistical mechanics by kinetic considerations which are usually associated with Boltzmann. One of the original points of Feynman's approach is the fact that equipartition is taken as a starting point to derive Maxwell's velocity distribution and the Boltzmann factor, rather than as a consequence. Equipartition could be inferred by putting together the expression of the gas pressure as a function of the mean kinetic energy—obtained by the classic Bernouilli [2, sec. X] reasoning—and the ideal gas law. However a *derivation* of equipartition requires something more. In particular it is necessary to show that if a mixture of gases of different masses is held in the same vessel, the mean kinetic energy per particle for each kind of gas is the same at equilibrium. The argument given by Feynman is not totally convincing, as he himself remarks:

> This argument, which was the one used by Maxwell, involves some subtleties. Although the conclusions are correct, the result does *not* purely from the considerations of symmetry that we used before, since, by going to a reference frame moving through the gas, we may find a distorted velocity distribution. We have not found a simple proof of this result.

It is my aim in the present note to provide such a simple proof—at the level of rigor of the remainder of Feynman's discussion. My argument is basically a refinement of the admittedly weak one put forward by Maxwell in his 1860 memoir [3], rather than the more sophisticated one introduced in the 1867 memoir *On the Dynamical Theory of Gases* [4]. Both papers are accessible in S. G. Brush's collection *Kinetic Theory* [5, vol. 1, n. 10; vol. 2, n. 1].

2. Maxwell's argument of 1867

In his 1867 paper, Maxwell considers the velocity distribution for particles of the two kinds at equilibrium. Let us denote by $\boldsymbol{v}_1$ the velocity of a particle of the first kind and by $\boldsymbol{v}_2$ that of one of the second kind. After the collisions, let us denote the respective velocities by $\boldsymbol{w}_{1,2}$. Then, at equilibrium, the number of collisions going from $(\boldsymbol{v}_1, \boldsymbol{v}_2)$ to $(\boldsymbol{w}_1, \boldsymbol{w}_2)$ should be balanced by those going from $(\boldsymbol{w}_1, \boldsymbol{w}_2)$ to $(\boldsymbol{v}_1, \boldsymbol{v}_2)$. Maxwell argues in the following way that the balance should be *detailed*, velocity pair by velocity pair (I slightly changed the notations):

> Suppose that the number of molecules having velocity $\boldsymbol{v}'$ increases at the expenses of $\boldsymbol{v}$. Then since the total number of molecules corresponding to $\boldsymbol{v}'$

> remains constant, $\boldsymbol{w}$ must communicate as many to $\boldsymbol{v}''$, and so on till they return to $\boldsymbol{v}$.
>
> Hence if $\boldsymbol{v}$, $\boldsymbol{v}'$, $\boldsymbol{v}''$ be a series of velocities, there will be a tendency of each molecule to assume the velocities $\boldsymbol{v}$, $\boldsymbol{v}'$, $\boldsymbol{v}''$, etc. in order, returning to $\boldsymbol{v}$. Now it is impossible to assign a reason why the successive velocities of a molecule should be arranged in this cycle, rather than in the reverse order. If, therefore, the direct exchange between $\boldsymbol{v}$ and $\boldsymbol{v}'$ is not equal, the equality cannot be preserved by exchange in a cycle.

If the velocities of particles of the two kinds are independent, and if we denote by $f_{1,2}(\boldsymbol{v})$ the respective velocity distributions, we have at equilibrium

$$f_1(\boldsymbol{v}_1)f_2(\boldsymbol{v}_2) = f_1(\boldsymbol{w}_1)f_2(\boldsymbol{w}_2). \tag{1}$$

But the only connection between the pairs $(\boldsymbol{v}_1, \boldsymbol{v}_2)$ and $(\boldsymbol{w}_1, \boldsymbol{w}_2)$ is that the total kinetic energy is conserved. Thus both sides of eq. (1) can only depend on the total kinetic energy. This implies that $f_i(\boldsymbol{v})$ $(i = 1, 2)$ can only depend on the kinetic energy of each particle, and moreover that it must be of the form

$$f_i(\boldsymbol{v}) \propto \mathrm{e}^{-\frac{\beta}{2}m_i v^2}, \tag{2}$$

where m_i is the mass of particles of kind i, and β is a positive constant. Equipartition follows immediately.

This is an argument of great elegance, but it is probably a bit too abstract for an introductory lecture. In particular, it focuses on a necessary condition for equilibrium, while it could be more appealing to consider at least hypothetically the approach to equilibrium. Such an argument was first considered by Maxwell in his 1860 memoir.

3. Maxwell's argument of 1860

In his 1860 paper, Maxwell considers the effect of one collision between one particle of kind 1 and one of kind 2, animated by velocities equal, in modulus, to the mean velocity of each kind, and whose directions are perpendicular to each other. Indicating by v_i $(i = 1, 2)$ the modulus of the velocity of the particle of kind i, let us denote by w_i $(i = 1, 2)$ the corresponding moduli after impact. Then, by solving the problem of impact between hard spheres in this geometry, Maxwell shows that

$$m_1 w_1^2 - m_2 w_2^2 = \left(\frac{m_1 - m_2}{m_1 + m_2}\right)^2 \left(m_1 v_1^2 - m_2 v_2^2\right). \tag{3}$$

Thus the difference between the kinetic energies of the two kinds of particles is reduced by such an impact, by a ratio that depends only on the masses of the two particles. Maxwell then argues that it should vanish at equilibrium.

S. G. Brush [6, § 10.4] makes the following comment:

> It seems amazing to me that Maxwell should have thought he was proving a tendency toward equalization of kinetic energies by this argument, or that any of his contemporaries who bothered to examine the argument in detail should

have accepted it. All Maxwell has done is to pick out one very special kind of collision for which the kinetic energies become more nearly equal and then claim that the same result will follow for *all* collisions.

It seems clear to me that one cannot hope to derive the tendency toward equipartition without some additional statistical assumptions: after all, microscopic reversibility stands in the way. But it *is* possible to refine this argument in order to show that if the velocity distribution of the particles is such that the center-of-mass motion is correlated with the relative motion of colliding particles, this correlation is reduced for the outgoing particles after the collision. Then, if the velocities of the colliding particles are independent (the molecular chaos hypothesis) this result implies that the difference between the kinetic energies of the particles of the two kinds are indeed reduced by collisions. This is explained in the next section.

4. Equipartition in a gas mixture

Let us consider a mixture of two gases, kind 1 with mass m_1 and kind 2 with mass m_2. We assume that the range of interactions among the particles is finite, and much smaller than the interparticle distance, so that it is safe to assume that the particles do not interact among themselves except for the very short time in which they collide. The collisions are elastic, and conserve the momentum. Let us now consider a collision between a particle of kind 1, animated by velocity $\boldsymbol{v}_1$, and one of kind 2, animated by velocity $\boldsymbol{v}_2$. Let us denote by $\boldsymbol{w}_1$ and $\boldsymbol{w}_2$ the respective velocities after the collision.

The laws of conservation of momentum and energy stipulate

$$m_1\boldsymbol{v}_1 + m_2\boldsymbol{v}_2 = m_1\boldsymbol{w}_1 + m_2\boldsymbol{w}_2; \tag{4}$$

$$\frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}m_1w_1^2 + \frac{1}{2}m_2w_2^2. \tag{5}$$

As a consequence of these relations, the absolute value of the relative velocity remains the same before and after the collision. Setting $\boldsymbol{V} = \boldsymbol{v}_2 - \boldsymbol{v}_1$ and $\boldsymbol{W} = \boldsymbol{w}_2 - \boldsymbol{w}_1$, we have

$$|\boldsymbol{W}| = |\boldsymbol{V}|. \tag{6}$$

Thus the effect of collisions, as seen in the center-of-mass frame, amounts to a change in the direction of the relative velocity. It is natural to assume that the great number of collisions that take part in the medium make the distribution of $\boldsymbol{V}$ isotropic, i.e., that the probability that the direction of $\boldsymbol{V}$ belongs to a solid angle $\mathrm{d}\Omega$ depends only on the size of the solid angle.

We now show that collisions can only reduce the correlation between $\boldsymbol{v}_{\mathrm{cm}}$ and $\boldsymbol{V}$.

Let us assume that, at a given time, there is a certain joint distribution $f(\boldsymbol{v}_{\mathrm{cm}}, V, \theta)$ of the center-of-mass velocity $\boldsymbol{v}_{\mathrm{cm}}$, the modulus V of the relative velocity and of the angle θ between $\boldsymbol{V}$ and $\boldsymbol{v}_{\mathrm{cm}}$ for molecule pairs that are about to collide. Thus one has

$$\langle \boldsymbol{v}_{\mathrm{cm}} \cdot \boldsymbol{V} \rangle = \int \mathrm{d}\boldsymbol{v}_{\mathrm{cm}} \int \mathrm{d}V \int \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi \; f(\boldsymbol{v}_{\mathrm{cm}}, V, \theta) \, v_{\mathrm{cm}} V \, \cos\theta.$$

Note that the assumed isotropy of $\boldsymbol{V}$ does not imply that $\langle\cos\theta\rangle = 0$, because $\boldsymbol{v}_{\rm cm}$ determines a special direction. On the other hand, it does imply that the distribution is invariant with respect to rotations around $\boldsymbol{v}_{\rm cm}$, i.e., that the distribution does not depend on ϕ.

Note that each collision leaves $\boldsymbol{v}_{\rm cm}$ and V unchanged, and thus its effect can be summarized by giving the direction (θ_1, ϕ_1), in polar coordinates, of the relative velocity $\boldsymbol{W}$ of the outgoing particles with respect to the relative velocity $\boldsymbol{V}$ of the ingoing ones. Invariance with respect to rotations around $\boldsymbol{V}$ intimates that the probability distribution density $P_V(\theta_1, \phi_1)$ of (θ_1, ϕ_1) does not depend on ϕ_1. On the other hand, $P_V(\theta_1, \phi_1)$ is determined only by the laws of the collision, and should satisfy galelean invariance: thus it cannot depend on $\boldsymbol{v}_{\rm cm}$. We can now evaluate the average of $(\boldsymbol{v}_{\rm cm} \cdot \boldsymbol{V})$ by integrating over the relative direction (θ_1, ϕ_1) of $\boldsymbol{W}$ with respect to $\boldsymbol{V}$, then on the relative direction of $\boldsymbol{V}$ with respect to $\boldsymbol{v}_{\rm cm}$, and finally over V and $\boldsymbol{v}_{\rm cm}$. Denoting by Θ the angle between $\boldsymbol{v}_{\rm cm}$ and $\boldsymbol{W}$, we have

$$\cos\Theta = \cos\theta\cos\theta_1 - \sin\theta\sin\theta_1\cos\phi_1. \tag{7}$$

This result can be obtained by considering figure 1. The simplest way is to write down the vector $\boldsymbol{W}$ as a function of (θ_1, ϕ_1), by setting the z-axis in the direction of $\boldsymbol{V}$, and then applying a rotation by an angle θ around the y-axis to the result. When we average

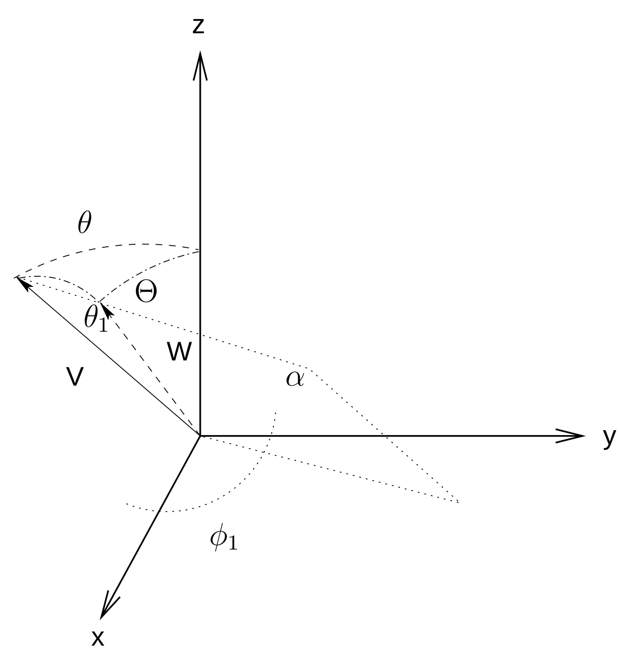

Figure 1. Particle scattering. The z-axis lies along $\boldsymbol{v}_{\rm cm}$ and the xz-plane is defined by $\boldsymbol{v}_{\rm cm}$ and $\boldsymbol{V}$. We define θ as the angle between $\boldsymbol{v}_{\rm cm}$ and $\boldsymbol{V}$. Then $\boldsymbol{V}$ and $\boldsymbol{W}$ define the plane α, which forms the angle ϕ_1 with the xz-plane. Then, θ_1 is the angle between $\boldsymbol{W}$ and $\boldsymbol{V}$. Thus the cosine of the angle Θ between $\boldsymbol{W}$ and $\boldsymbol{v}_{\rm cm}$ is given by $\cos\theta\cos\theta_1 - \sin\theta\sin\theta_1\cos\phi_1$.

upon ϕ_1, the second term vanishes. Thus, when $\boldsymbol{v}_{\rm cm}$ and V are fixed, we have

$$\langle\cos\Theta\rangle = \langle\cos\theta\cos\theta_1\rangle = \langle\cos\theta\rangle\langle\cos\theta_1\rangle,$$

and thus

$$|\langle \cos \Theta \rangle| \leq |\langle \cos \theta \rangle| \,. \tag{8}$$

This holds true also when we average over $\boldsymbol{v}_{\rm cm}$ and V. Thus

$$|\langle \boldsymbol{v}_{\rm cm} \cdot \boldsymbol{W} \rangle| \leq |\langle \boldsymbol{v}_{\rm cm} \cdot \boldsymbol{V} \rangle| \,. \tag{9}$$

Since collisions reduce correlations, we may conclude that correlations should vanish at equilibrium:

$$\langle \boldsymbol{v}_{\rm cm} \cdot \boldsymbol{V} \rangle_{\rm eq} = 0. \tag{10}$$

From now on, we can follow Feynman's argument. Since

$$\boldsymbol{v}_{\rm cm} = \frac{m_1 \boldsymbol{v}_1 + m_2 \boldsymbol{v}_2}{m_1 + m_2},$$

we have

$$\langle \boldsymbol{v}_{\rm cm} \cdot \boldsymbol{V} \rangle_{\rm eq} = \frac{\langle m_2 v_2^2 - m_1 v_1^2 \rangle_{\rm eq} + (m_2 - m_1) \langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle_{\rm eq}}{m_1 + m_2}. \tag{11}$$

The right hand side is proportional to the difference in kinetic energies of the two kinds of particles if we assume that the velocities of the colliding particles are independent, so that $\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle_{\rm eq}$ vanishes. Now this is one form of the celebrated *molecular chaos hypothesis*. If it holds at any given time, we have just shown that the difference between the mean kinetic energies is reduced. If it holds at equilibrium, the only possibility is that the difference vanishes:

$$\frac{1}{2} m_1 \left\langle v_1^2 \right\rangle_{\rm eq} = \frac{1}{2} m_2 \left\langle v_2^2 \right\rangle_{\rm eq}. \tag{12}$$

It is satisfactory to see that the argument does not hold in one dimension: in this case the only recoil possibility corresponds to $W = -V$, and thus $|\langle \cos \theta \rangle| = 1$.

5. Discussion

From a didactical point of view, I guess that the best course would be to first introduce Maxwell's symmetry arguments leading to the velocity distribution, and then to demostrate by the present argument or a similar one that the distribution is left invariant by collisions, provided that some form of molecular chaos hypothesis is made. It would be nice to point out that without such an hypothesis it will always be possible to arrange the molecules in such a way as to *increase* the kinetic energy difference, e.g., by reversing the velocities of the particles outgoing a collision. This should clarify the different roles of mechanical laws and statistical assumptions in the derivation of the basics of statistical mechanics.

Acknowledgments

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